

# Development of High Throughput Methods for Materials Flammability Research

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Combinatorial Methods Center

Combinatorial Methods  
Workshop

# Home Fires

- 4,000 Deaths/Year  
in US Home Fires - highest of  
Developed Countries
- 37 % from Upholstered  
Furniture Mattress and Bedding

Fire Statistics: National Fire Protection Assoc. 1996



**3 minutes to flashover !**

NIST Bunk bed Study: [www.fire.nist.gov](http://www.fire.nist.gov)

# General Flame Retardant Approaches for Polymers

## I- Gas Phase Flame Retardants

- Reduce Heat of Combustion ( $\Delta H_c$ ) by scavenging reactive free radicals, resulting in incomplete combustion.
- Inherent Drawbacks: Negative Public Perception!

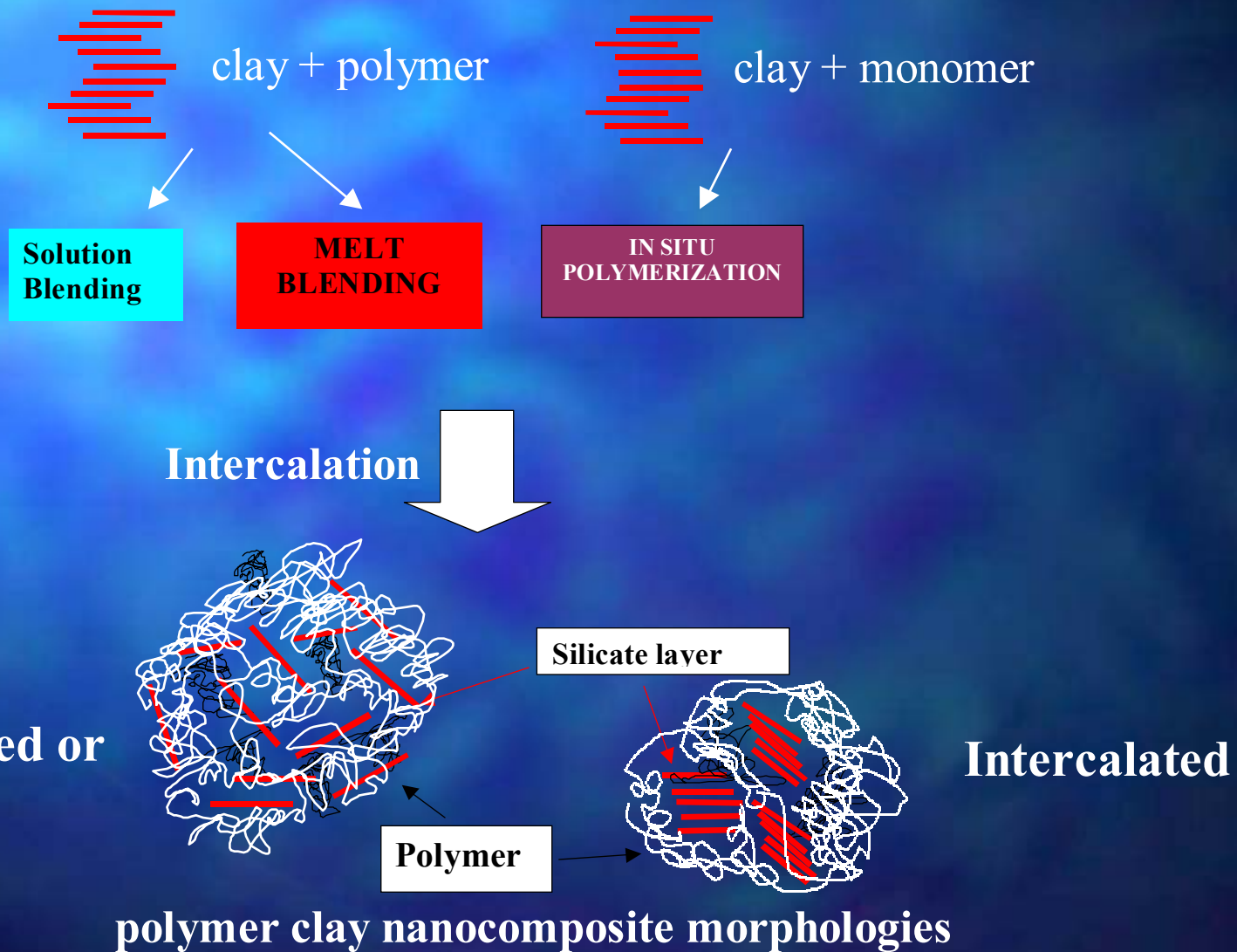
## II- Endothermic Flame Retardants

- Function in Gas Phase and Condensed Phase
- Via endothermic release of  $H_2O$ , polymer cooled and gas phase diluted.
- Inherent Drawback: High loadings (30-50%) degrade mechanical properties.

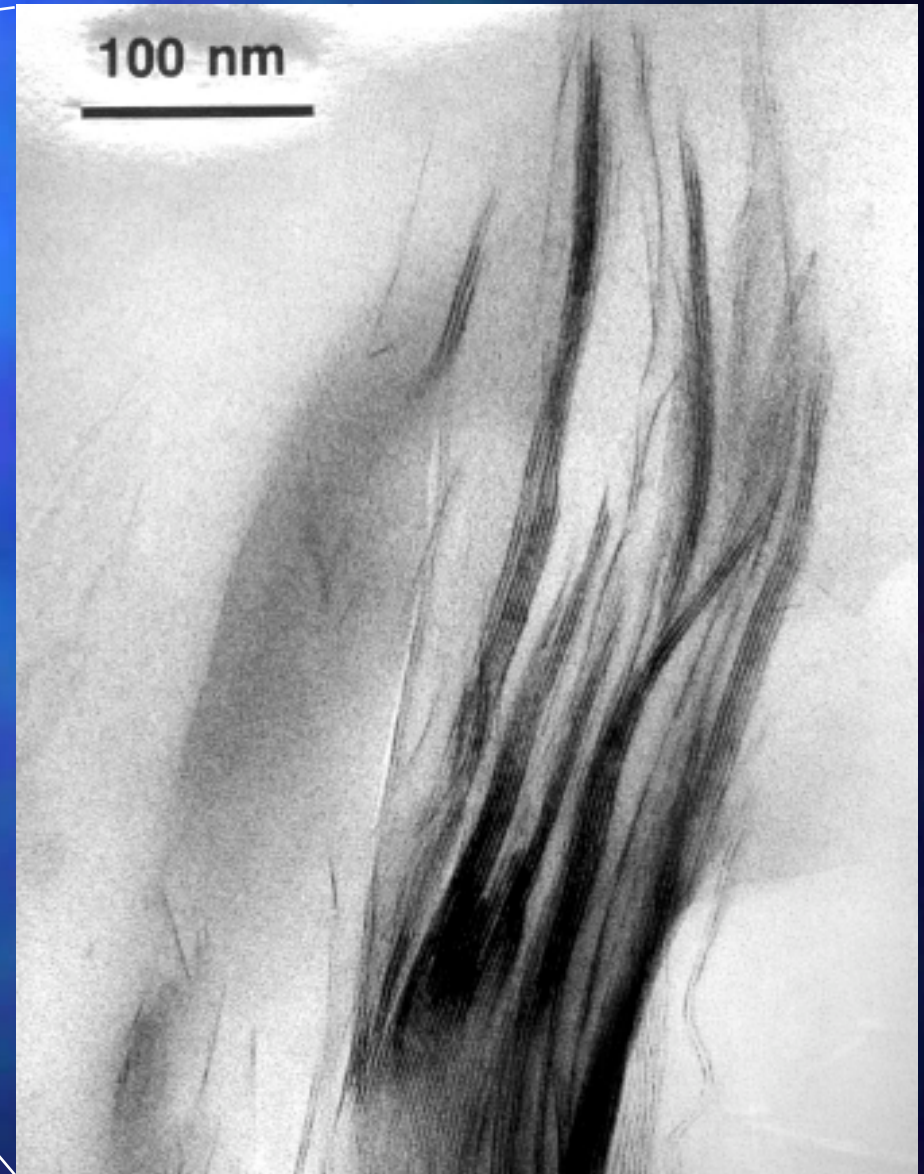
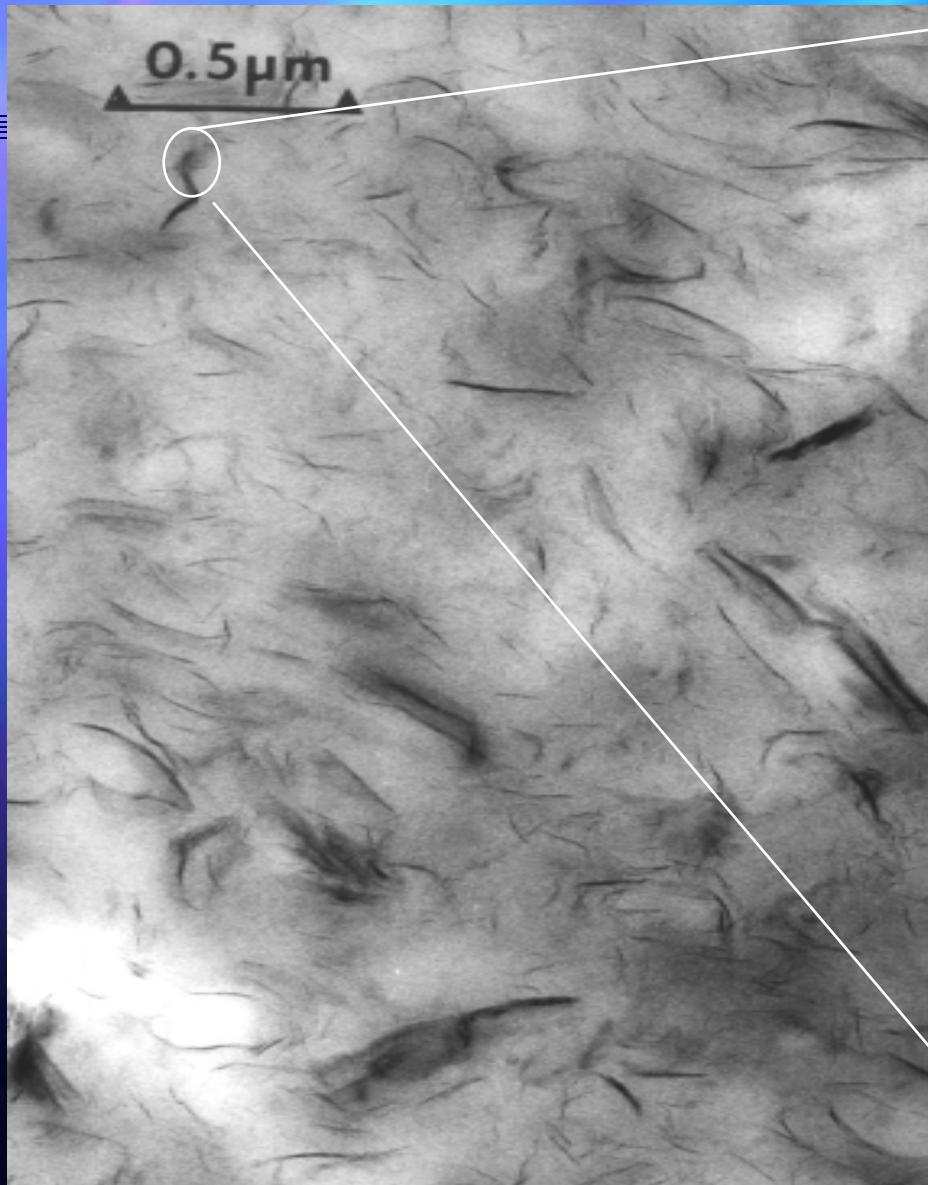
## III- Char Forming Flame Retardants

- Operate in Condensed Phase
- Provides thermal insulation for underlying polymer and a mass transport barrier, preventing or delaying escape of fuel into the gas phase.

# Preparation of Polymer Clay-nanocomposites



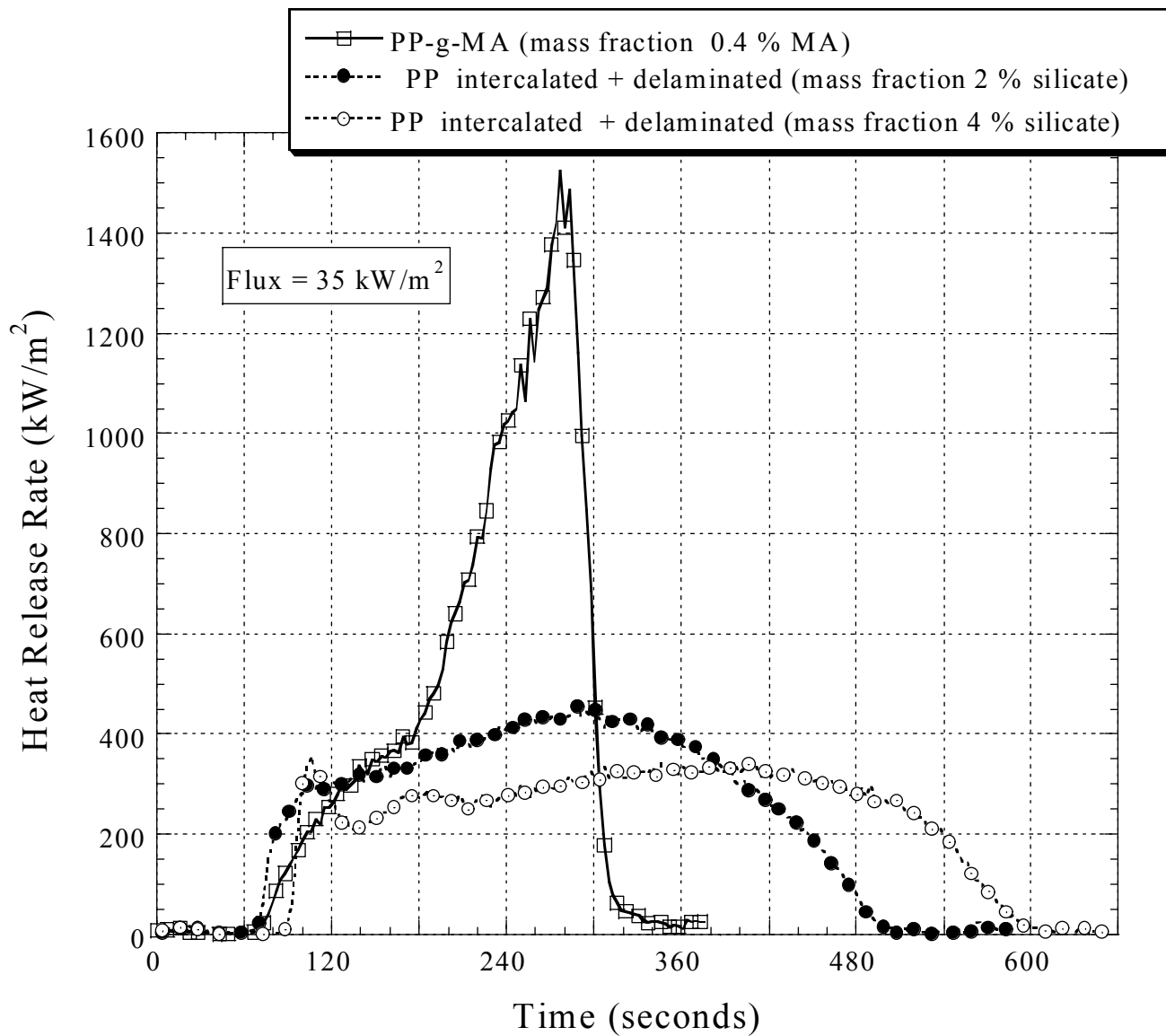
# PP-clay Nanocomposite: TEM



# Cone Calorimeter



# PP-clay Nanocomposite: Cone Calorimetry



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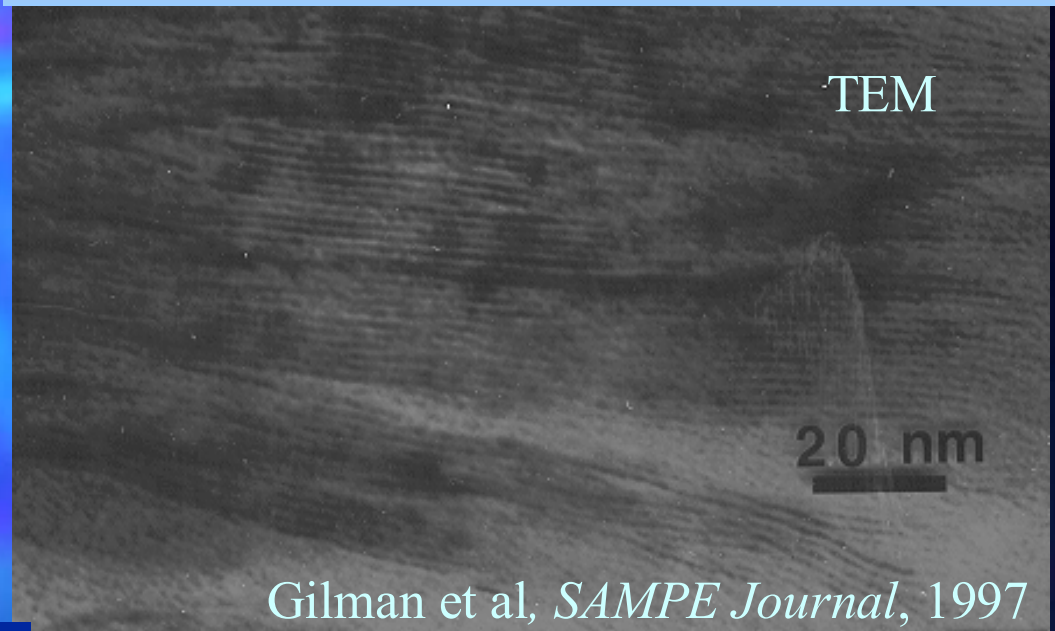
# *Flammability of Polymer Clay Nanocomposites Consortium*

**~1997 - 2000**

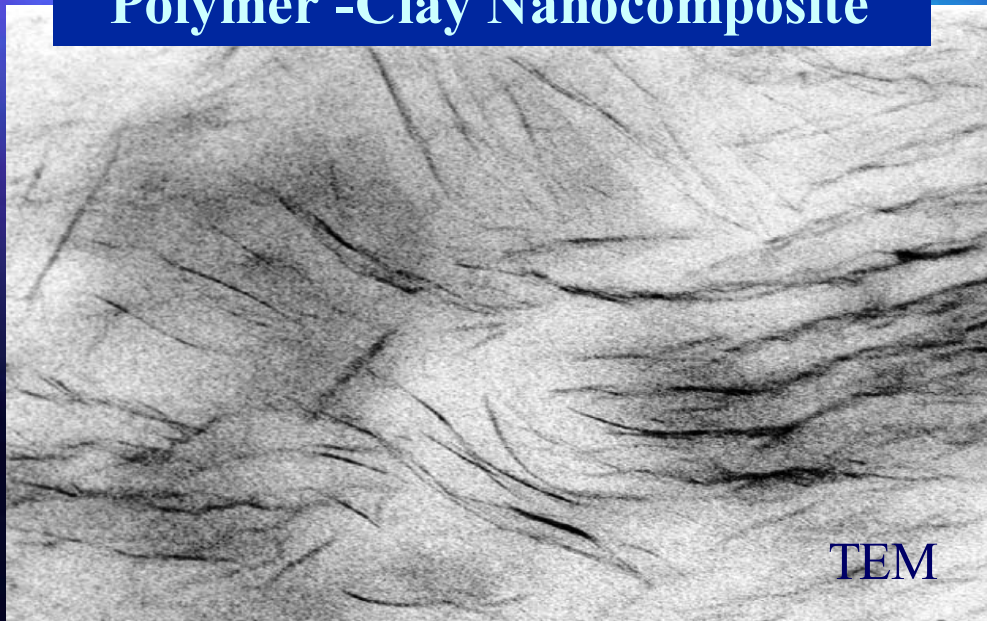
**Year One Annual Report: Gilman, et al, *NISTIR 6531***

# Flame Retardant Mechanism

## Clay reinforced Carbonaceous Char



## Polymer -Clay Nanocomposite



Combustion

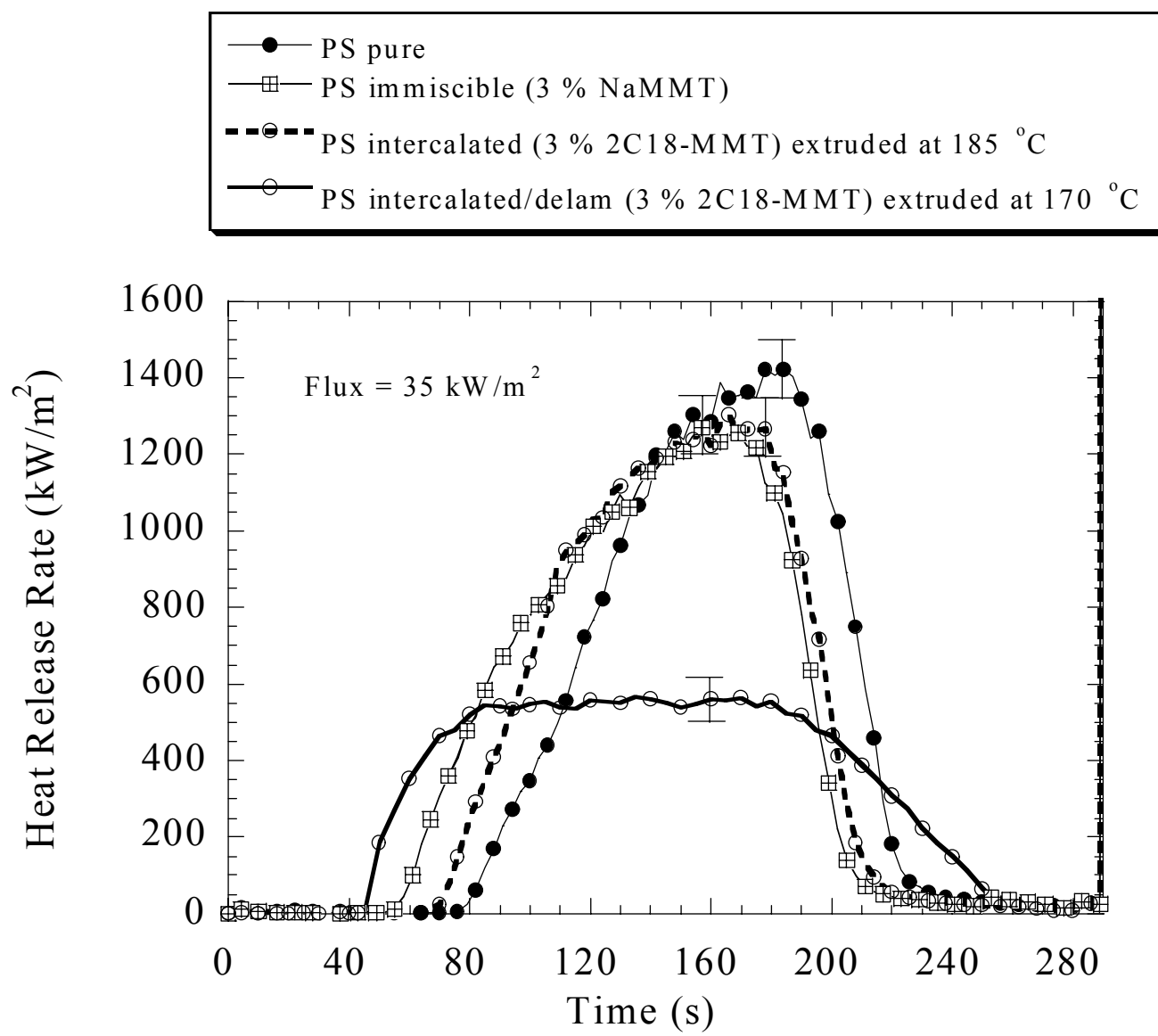
Reduced Flammability  
with  
Improved  
Mechanical Properties

# **Nanocomposites using Nano-Silicas and POSS Additives**

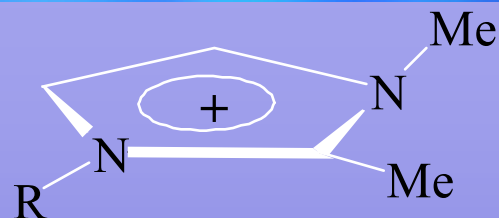
# Nanocomposite Issues

- Nano-dispersion
- Ammonium degradation
- Polymer degradation

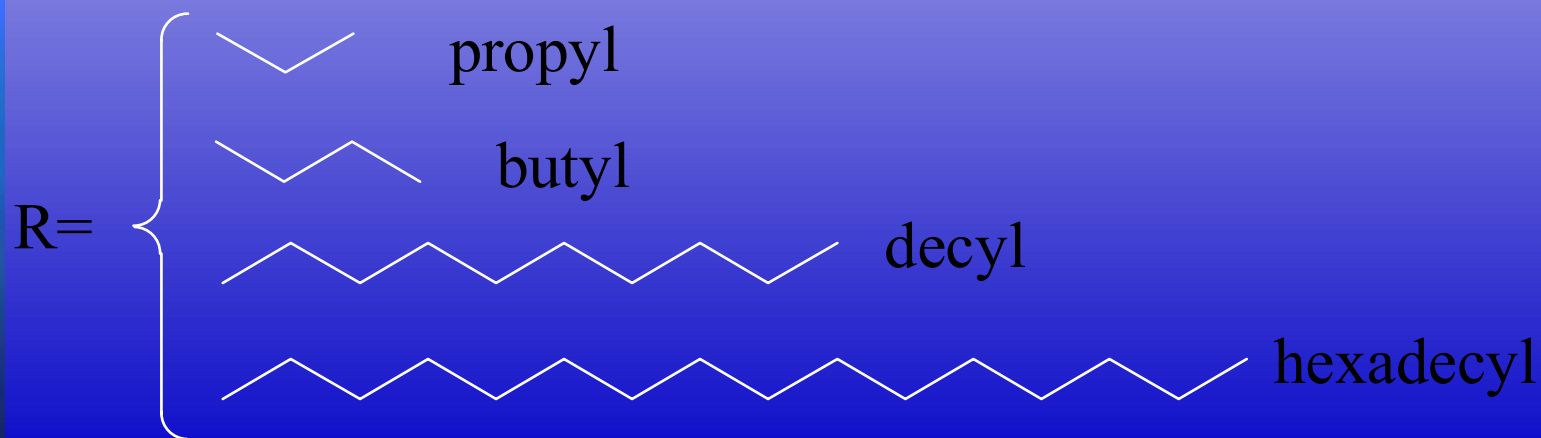
# Cone Calorimeter Heat Release Rate Data



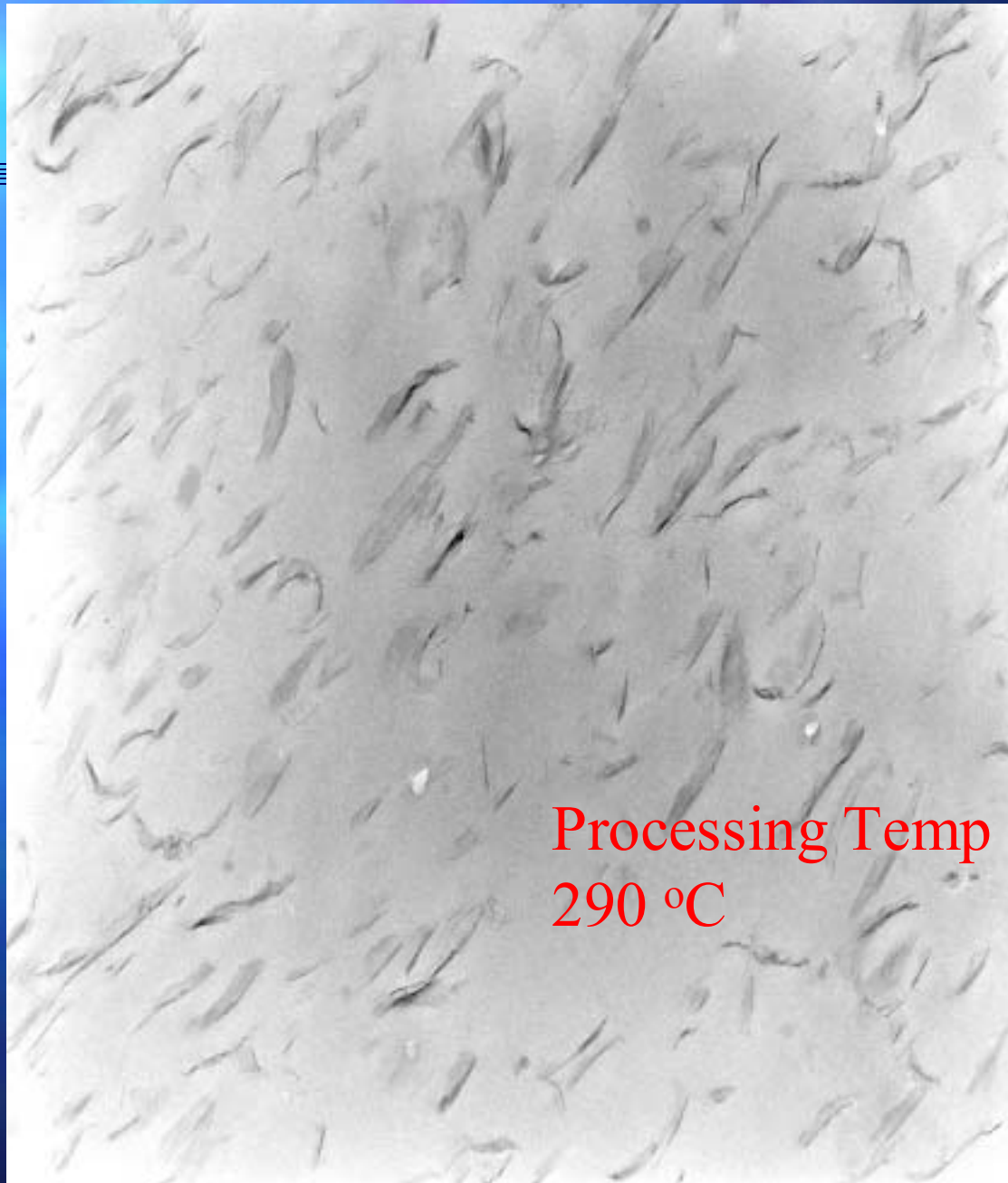
# Imidazolium- Salts



## Dimethyl alkyl imidazolium salts



# PET/DMHDIM-MMT Nanocomposite



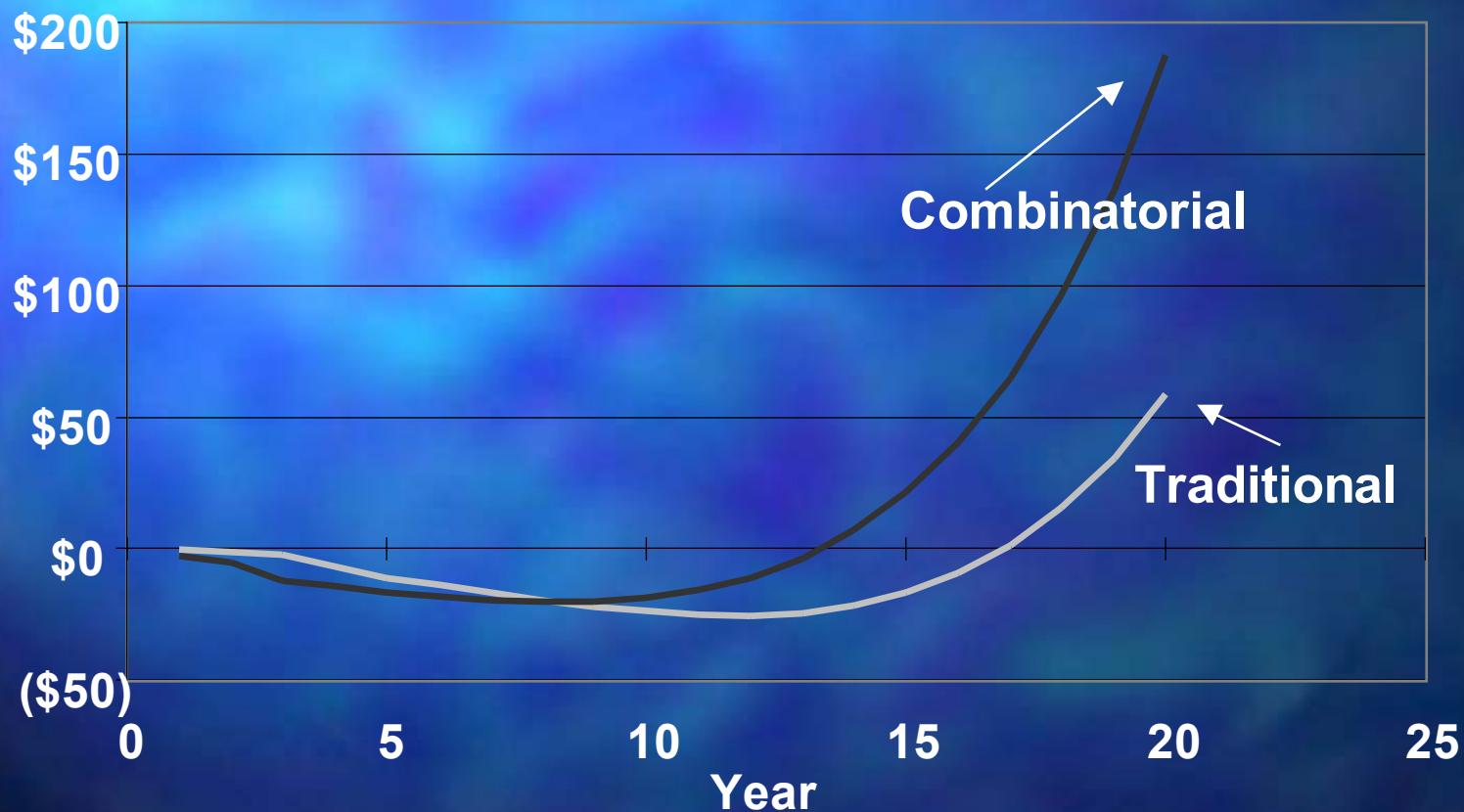
Processing Temp  
290 °C

# Parameter Space ( $\sim 10^6$ Experiments) for Polymer Nanocomposites

Polymer	Nano-additive	Counter-Ion	Organic Treatment	Processing Conditions	Other additives	Flame Retardant
PE PP PS PA6 PU PVC PC PEO PMMA EVA	MMT Mica Hectorite Saponite Laponite silica	Na Ca Cu Fe...	Alkylammonium Imidazolium Crown Ether Silated Carboxylate	Temperature Shear Residence time	Stabilizers Processing UV Antioxidant Fillers Pigments	Phosphate Halogenated Silicon Based
$\sim 10$	$\sim 5$	$\sim 5$	$\sim 10$	$\sim 10$	$\sim 10$	$\sim 10$

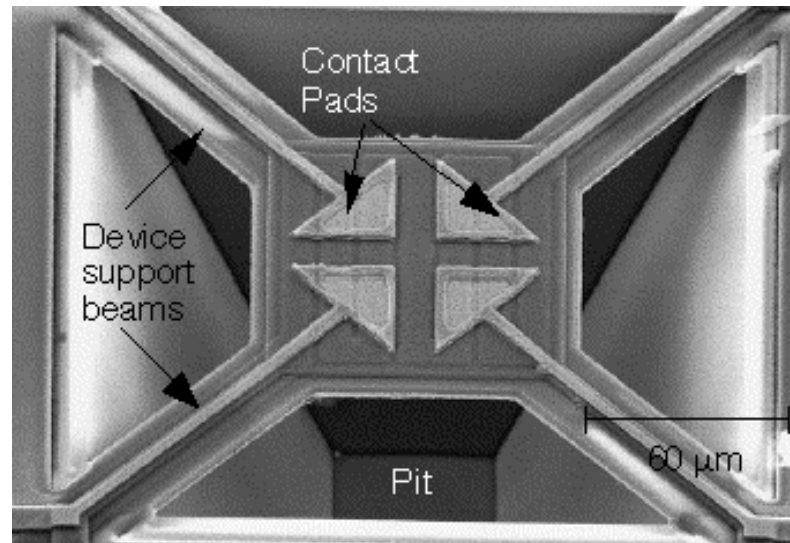
# High Throughput Flammability Methods

Cumulative Earnings  
"Generic" Plastics Development Program

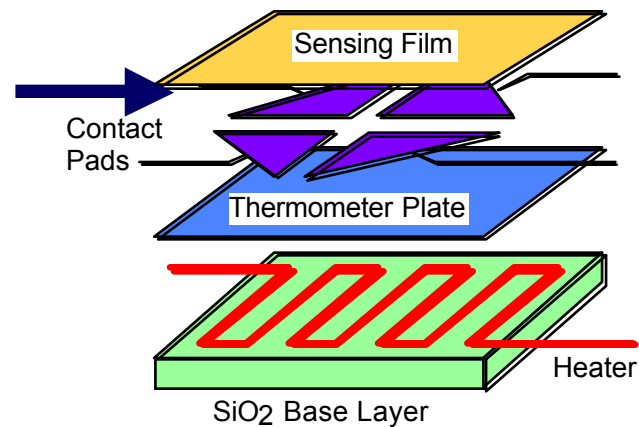


J. Busch, IBIS corp.

# Microhotplates



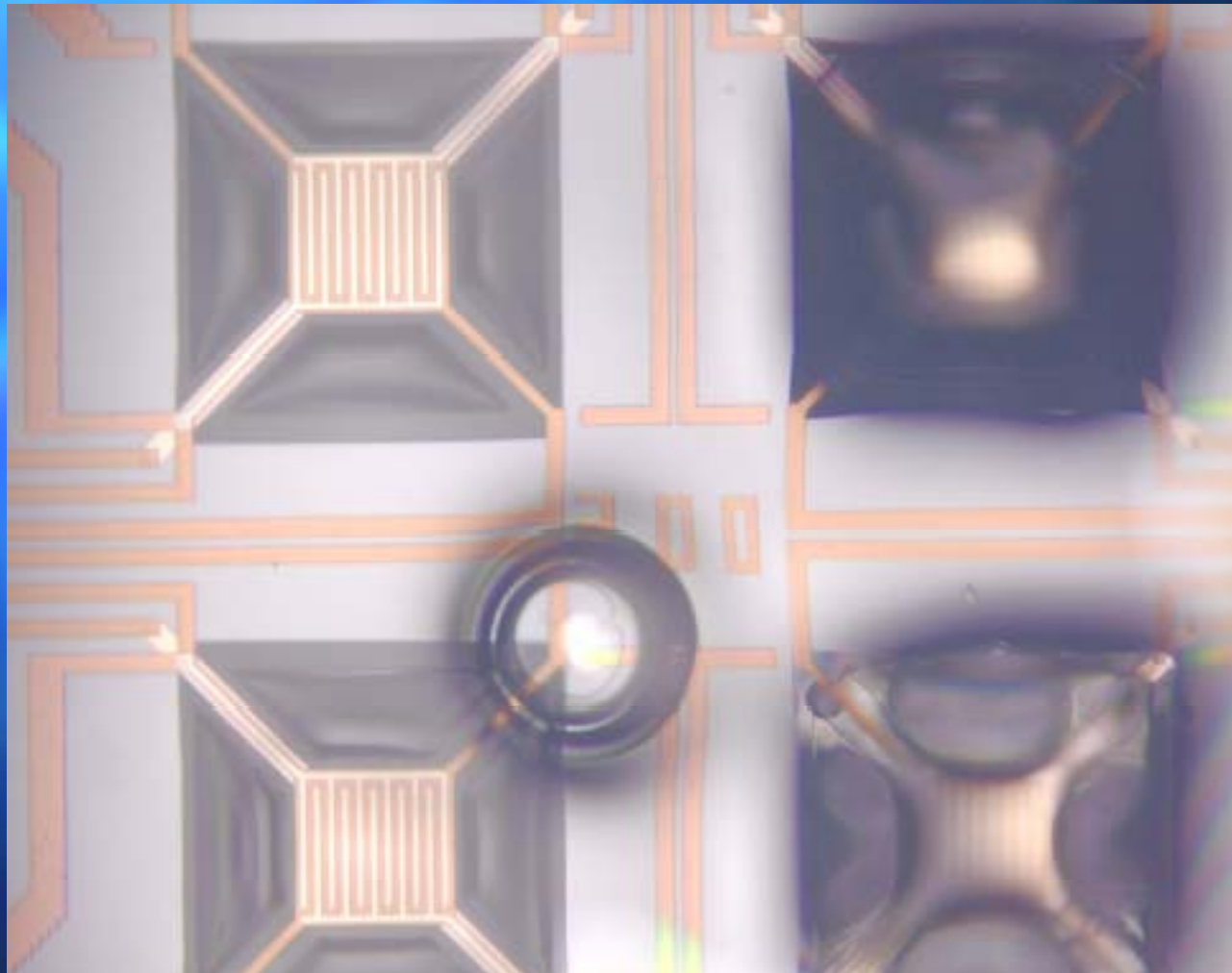
Coat sensing film with  
test material



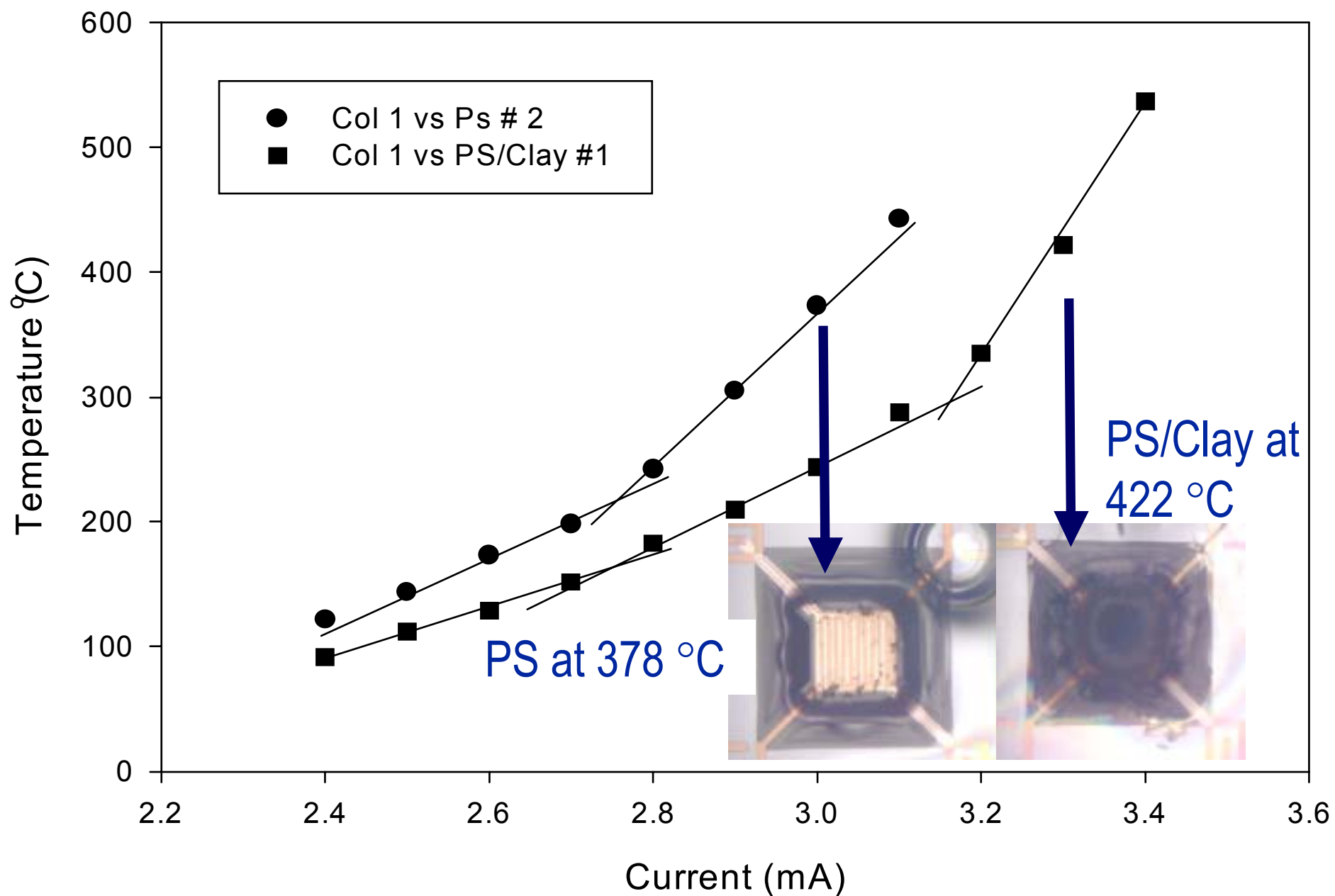
Correlate changes in  
power demand needed to  
maintain the specified  
heating rate with mass  
loss from degrading  
polymer

# Microhotplate Sample Preparation

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# Microhotplate Flammability Screening

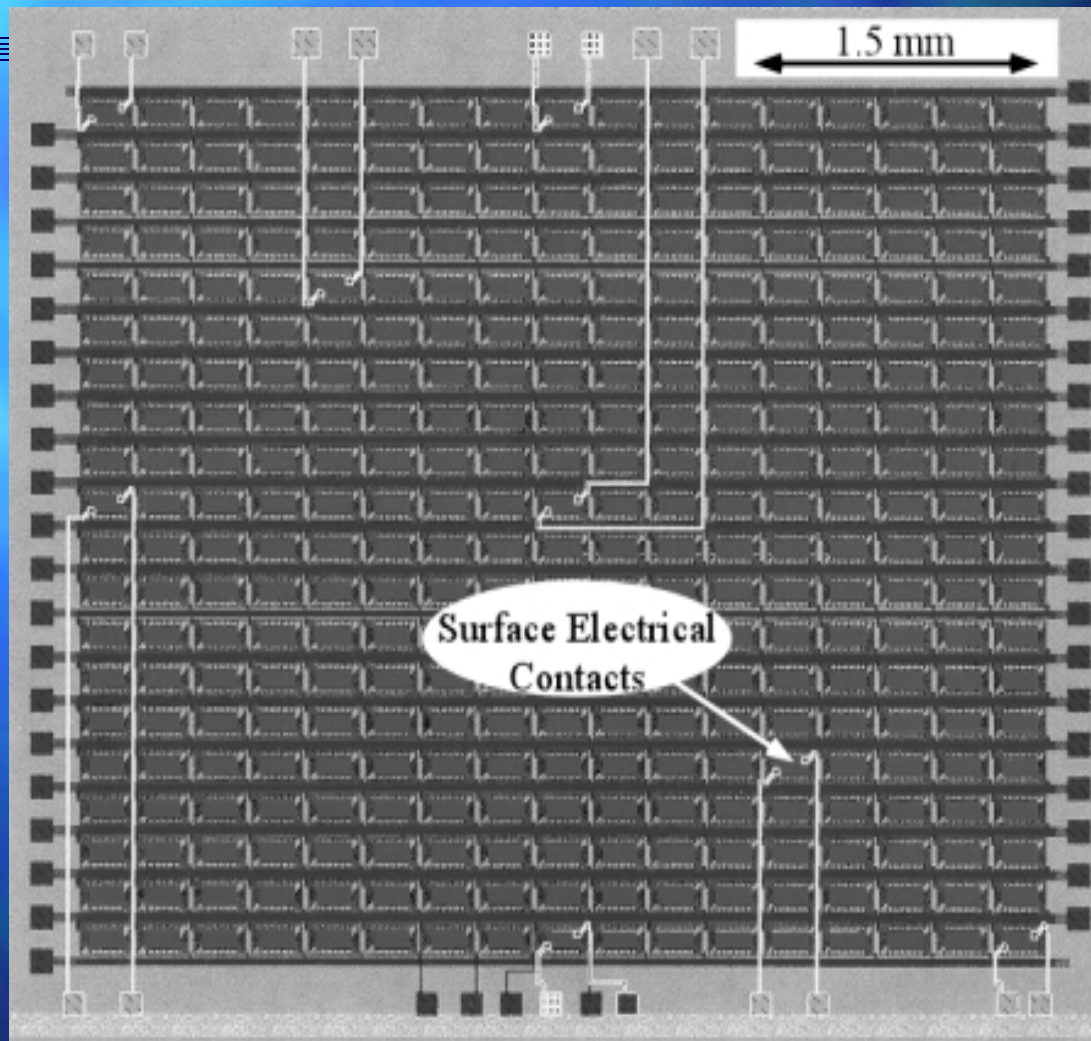


# Microhotplate Sample Preparation



According to MicroFab Technologies, drop volumes as low as 20 pL can be dispensed.

# Microhotplate Array (17 X 20)



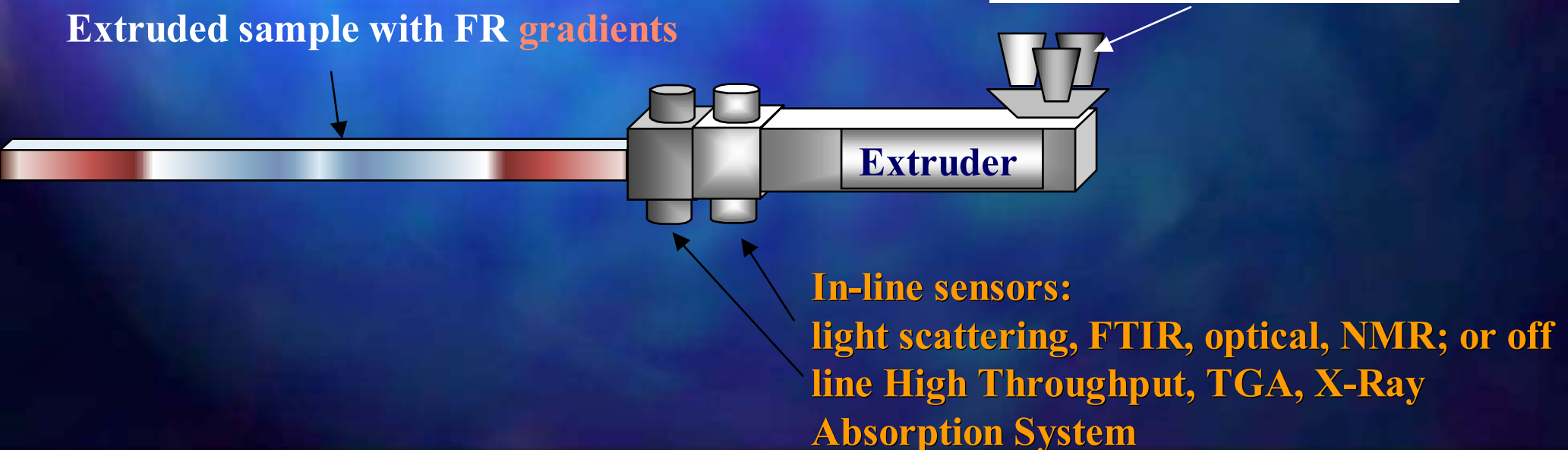
High-throughput flammability screening on small ( $\sim 1 \mu\text{g}$ ) samples

# Extrusion of Gradient Samples



**Gravimetric feeders**

Extruded sample with FR **gradients**

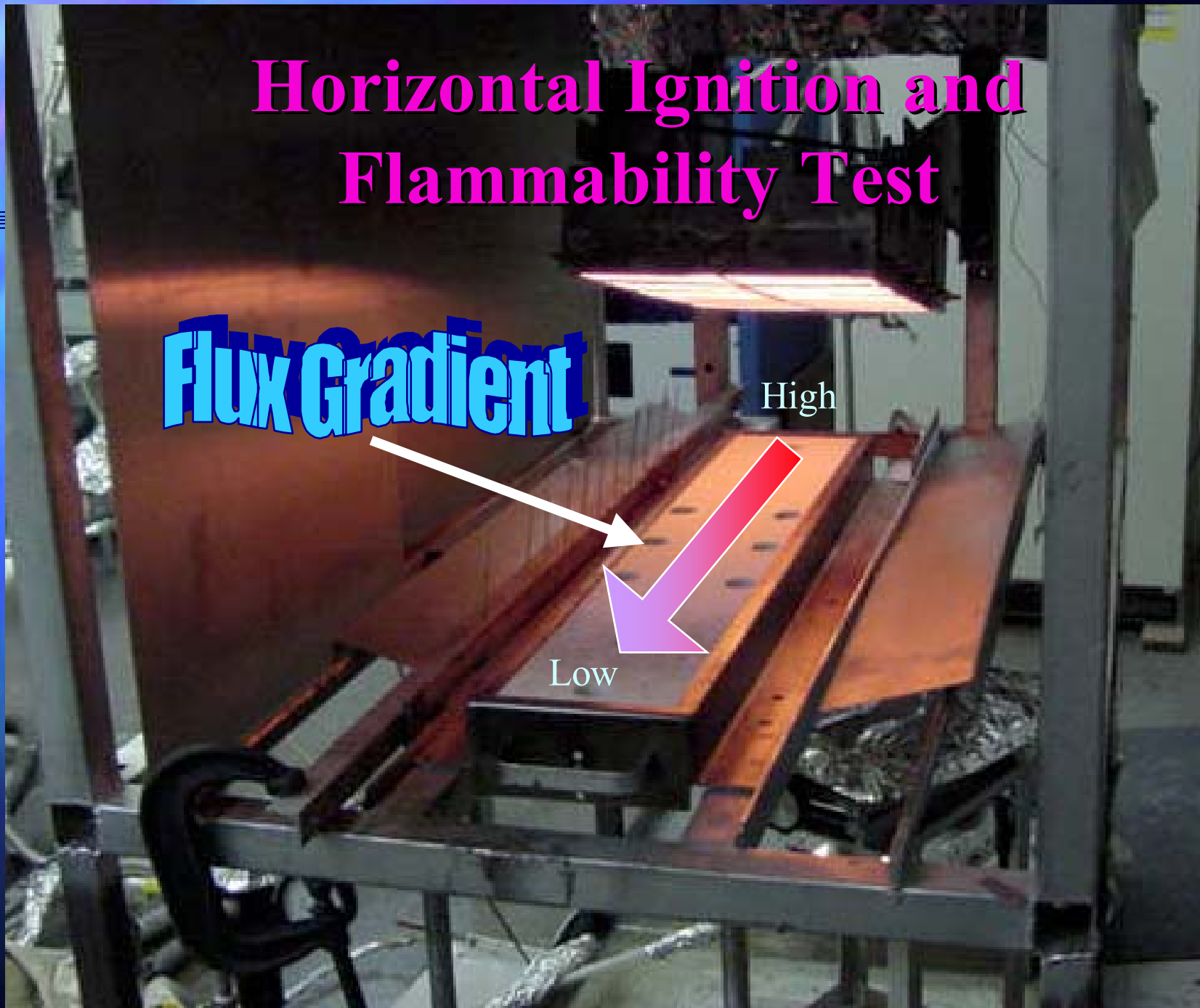


# Horizontal Ignition and Flammability Test

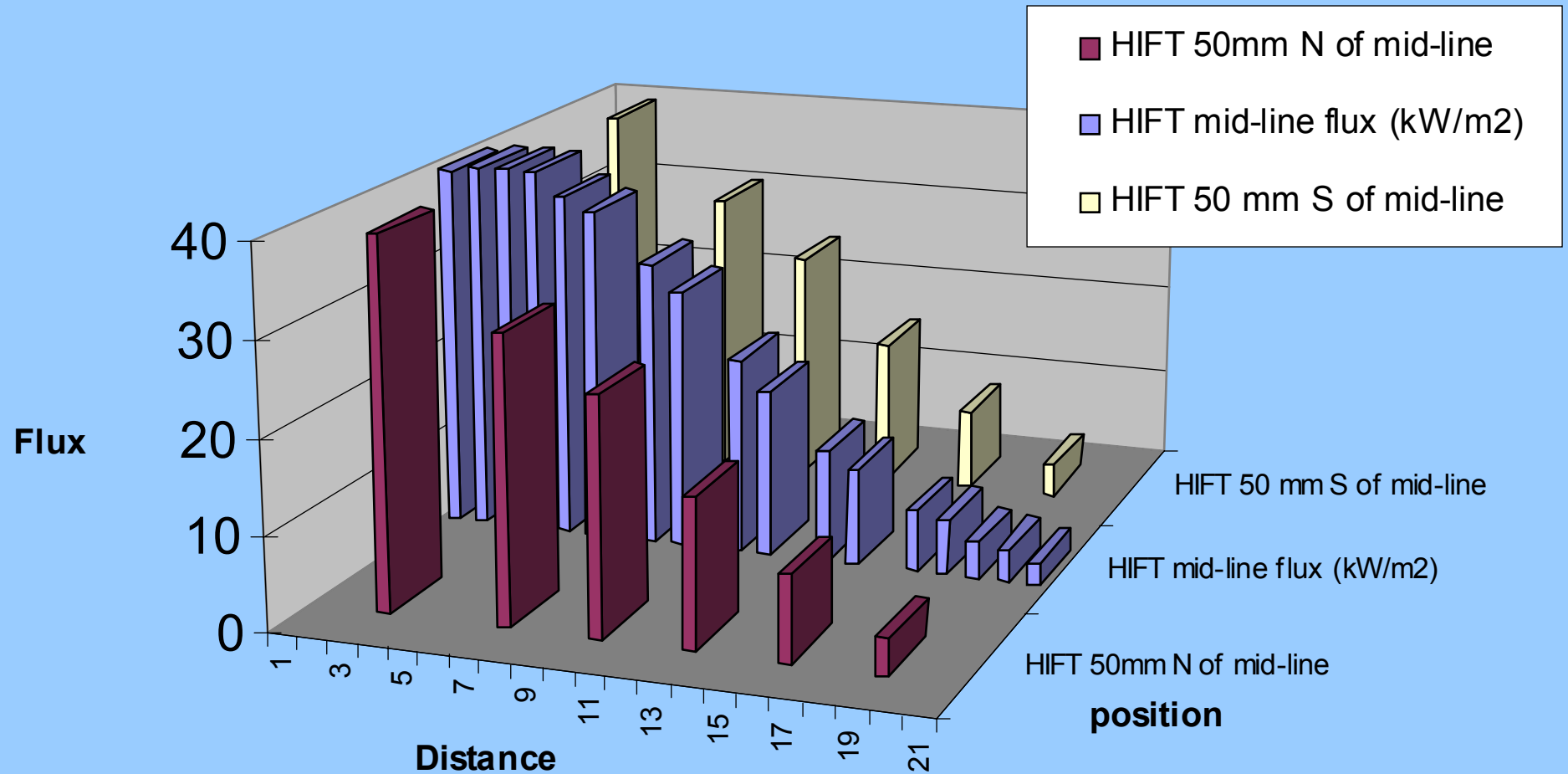
Flux Gradient

High

Low



# Flux Gradient in HIFT



# Horizontal Ignition and Flammability Test



# Gradient Flux Test



# HIFT



# HIFT

## Different Critical Fluxes for Flame-Spread

PS/APP-PER



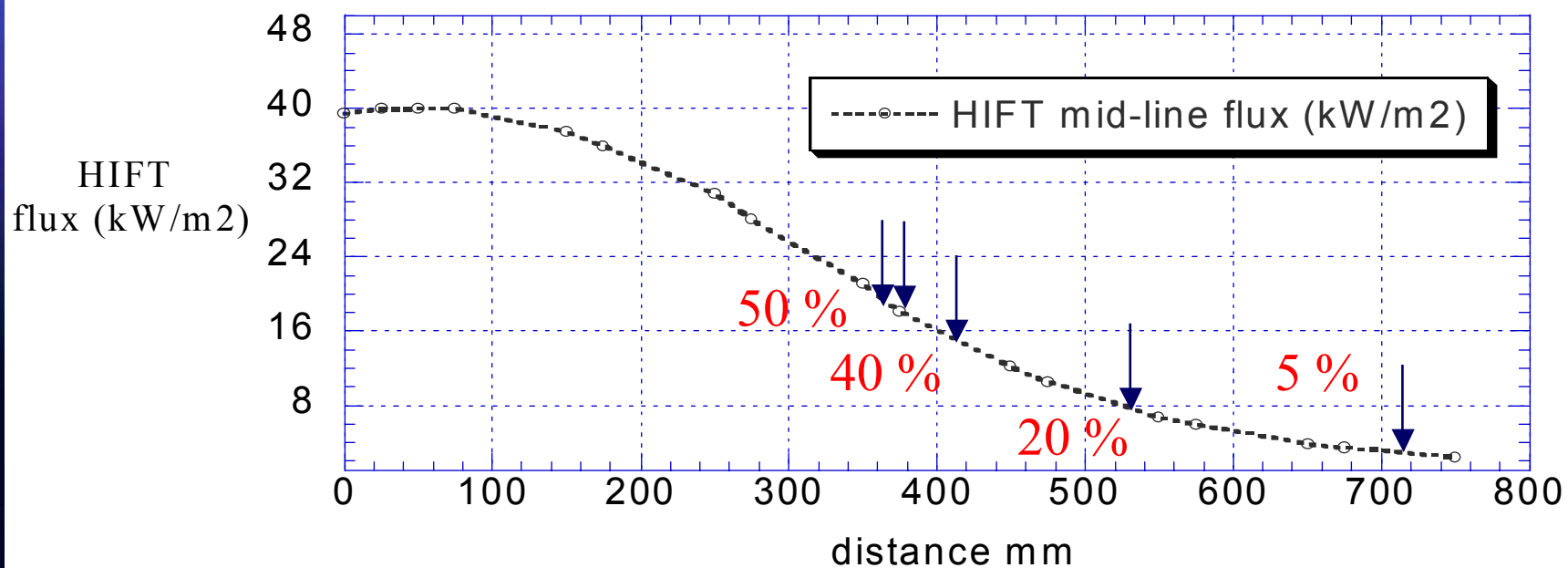
50 %

50 %

40 %

20 %

5 %

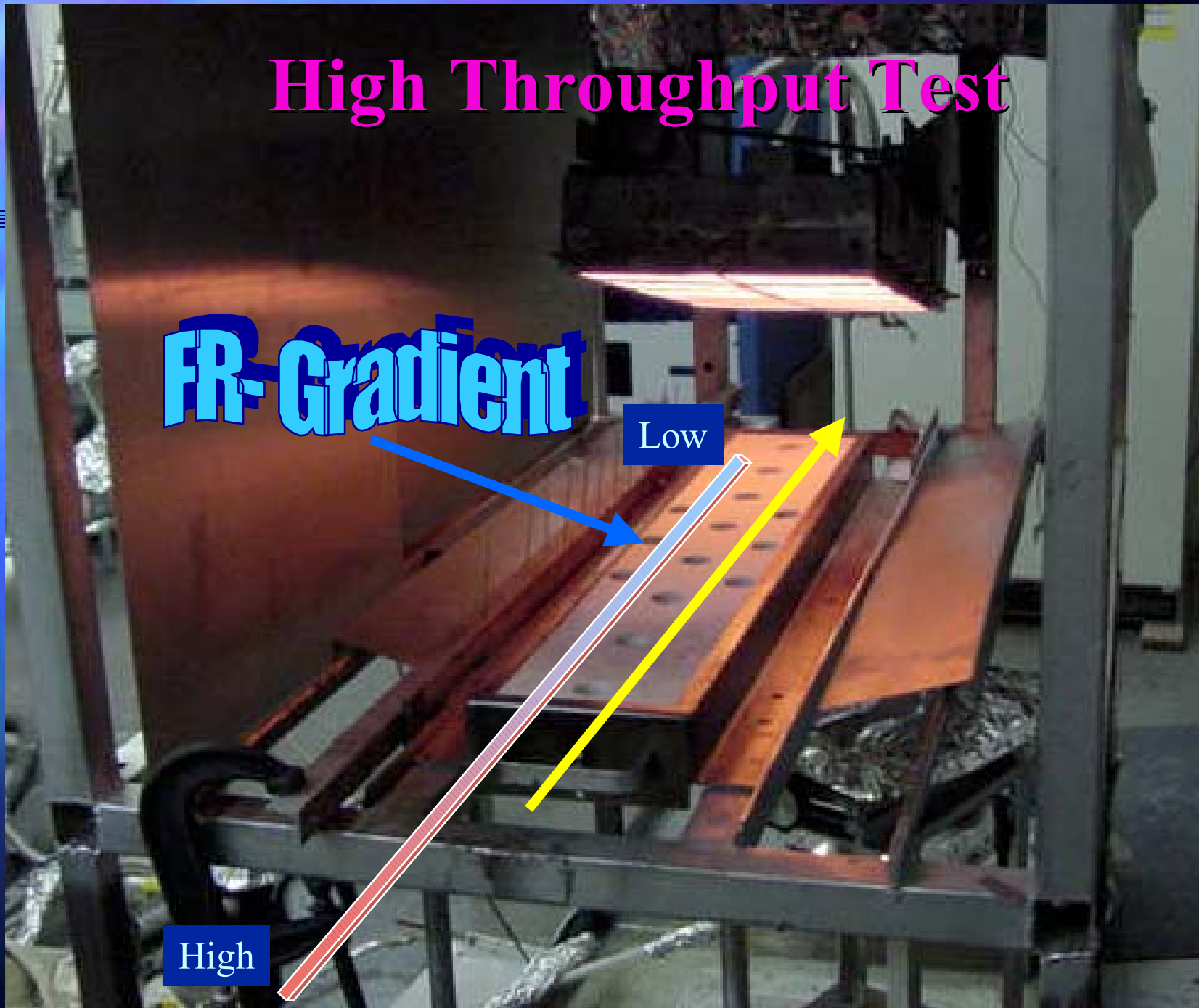


# High Throughput Test

FR-Gradient

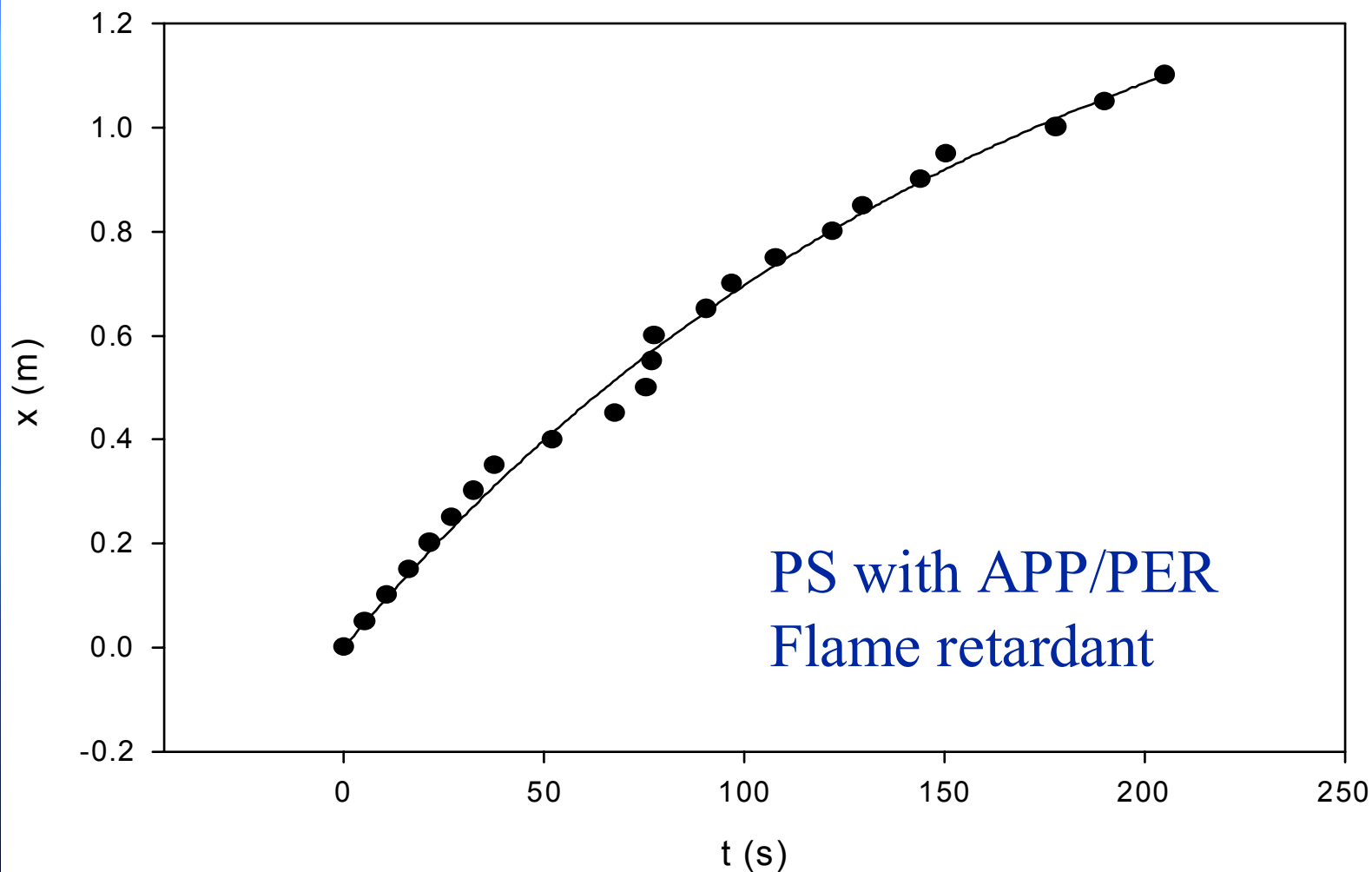
Low

High

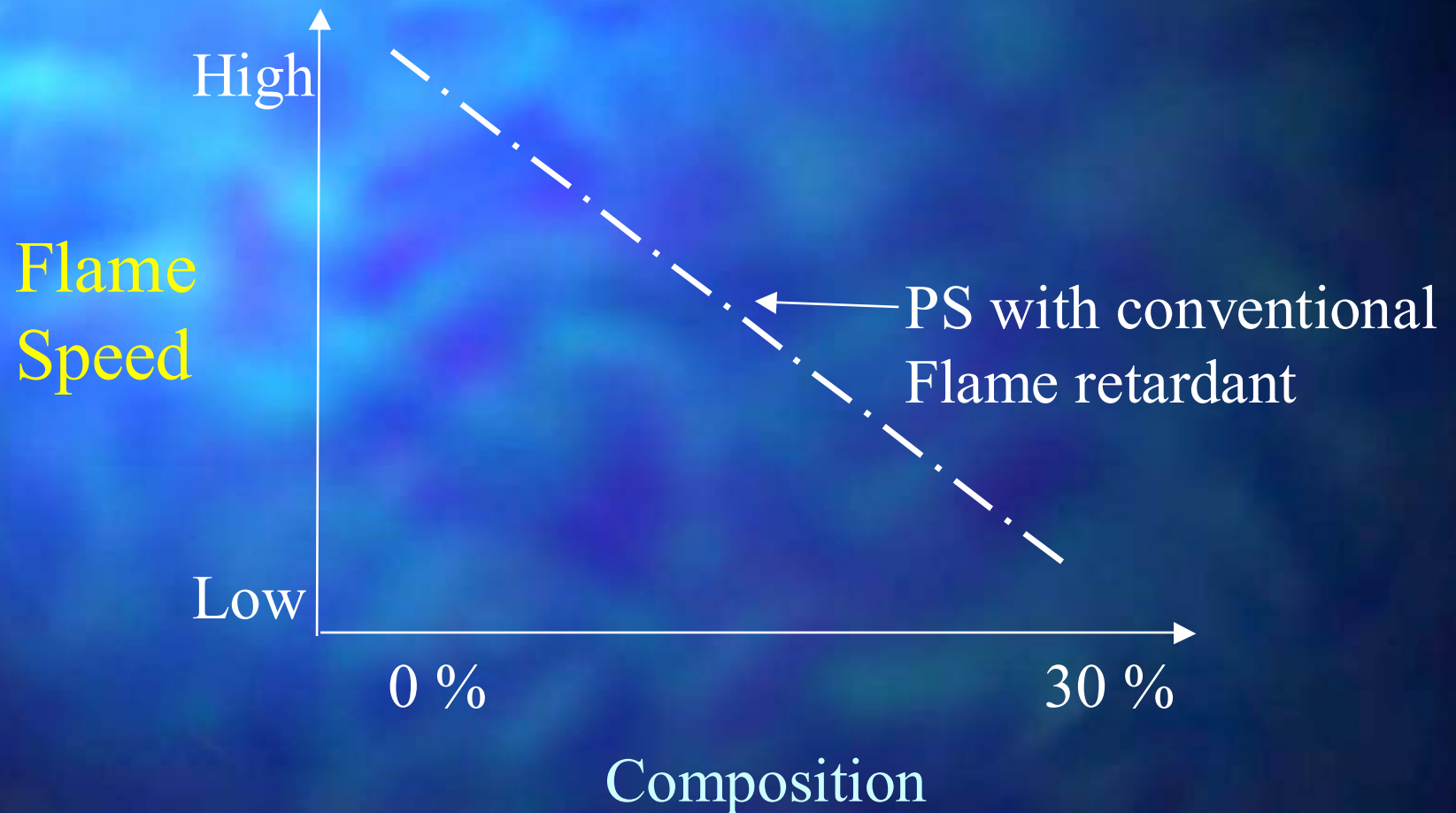


# High Throughput Test

Progression of Flame Front



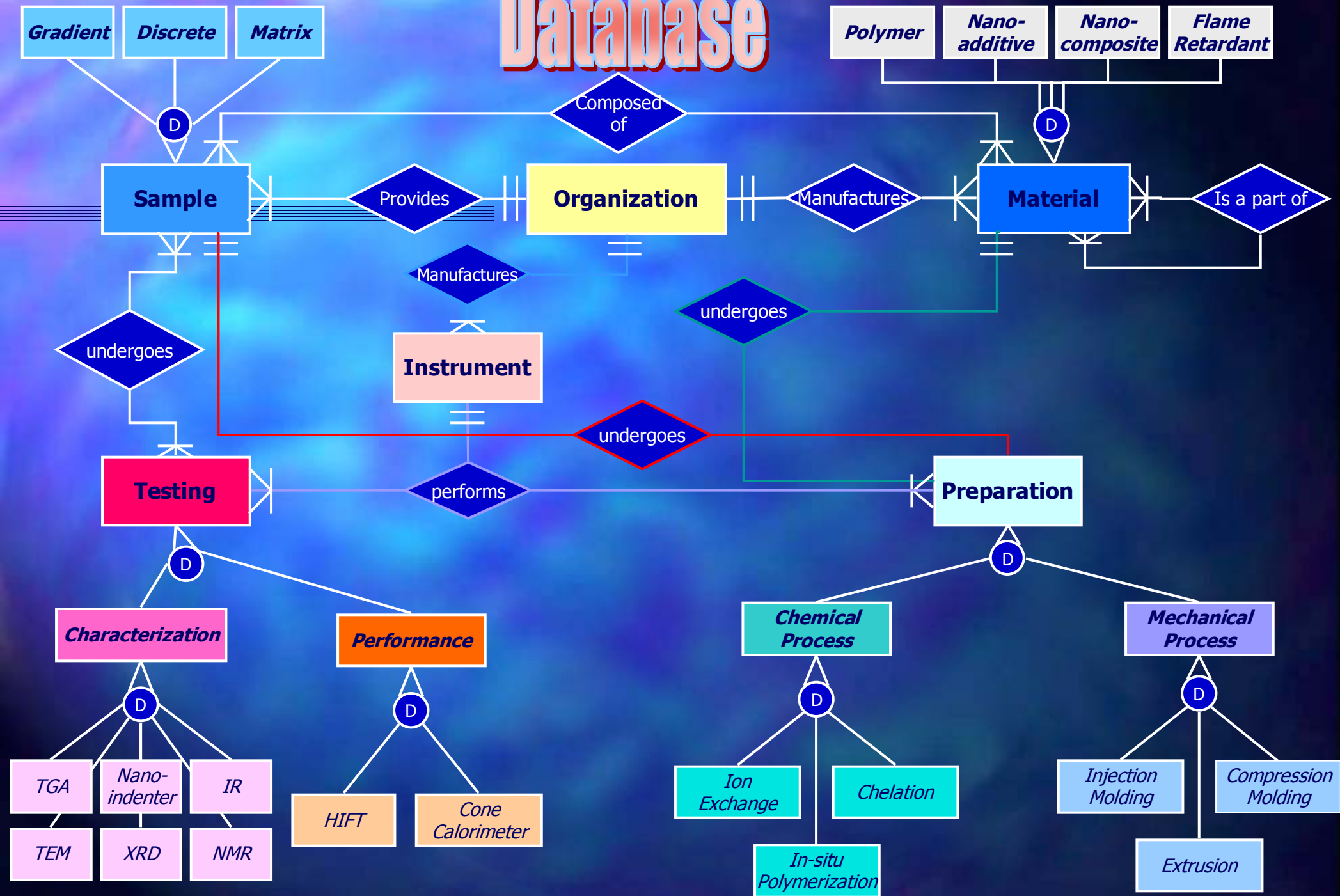
# High Throughput Test



# Conventional vs High Throughput Flammability Measurements

<i>Method</i>	<i>Repeatability (+/-)</i>	<i>Data-sets/day</i>	<i>Data Quality</i>
UL 94 V	Poor ( 50%)	2-3	Qualitative
Cone	Excellent (5%)	2-3	Multi- parameter Highly Quantitative
HIFT using gradient samples	Excellent (5%)	100's	Quantitative

# Database



# Conclusions

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By combining nanotechnology with high-throughput experimentation, we can maximize the effect of additives and thereby provide industry with a powerful tool for the development of a new generation of high performance, low flammability materials.

# Combinatorial Methods Center at NIST

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## **New Consortium: High-Throughput Methods for Flammability**

### **Team Project**

will work with project teams, consisting of 3 or more companies, to develop generic tools for high-throughput formulation, characterization, and flammability performance screening of materials and fire retardant systems.

# RESEARCH TEAM

**Marc Nyden, Rick Davis, John Shields, Walid Awad,  
Takashi Kashiwagi, Richard Harris, Lori Brassell, Kathy Butler, Michael Smith, Roy McLane  
BFRL/NIST**

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**<sup>3</sup> Naval Academy, Annapolis, MD**

**Advanced Technology Program -Monitored by John Hewes and Felix Wu**

**FAA, Richard Lyon at William J. Hughes Technical Center** (Interagency Agreement DTFA03-99-X-90009)

**Air Force Office of Scientific Research (ISSA - AFOSR- ISSA-01-0001 )**

# Materials and Products Group

Michael Smith, Richard Harris, Takashi Kashiwagi, Tom Ohlemiller, Marc Nyden  
Rick Davis, Kathy Butler, Greg Linteris, Lori Brassell, John Shields, Ruth Perkins,  
Wes Demory, David Wentz, Walid Awad,

